

Alkylation of α,α' -Dicyano-*p*-xylene

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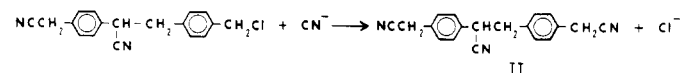
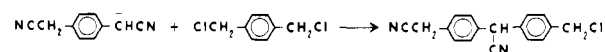
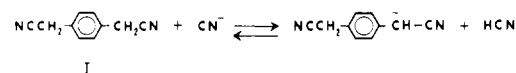
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The reaction of α,α' -dichloro-*p*-xylene with cyanide ion yields, in addition to the expected α,α' -dicyano-*p*-xylene, a trinitrile, 1,2-di(4-cyanomethylphenyl)-1-cyanoethane.

THE ALKYLATION of phenylacetonitriles with various halides in the presence of strong base has been amply documented (2, 4). It does not seem as widely appreciated that cyanide ion is a sufficiently strong base to effect the alkylation reaction and that alkylation can occur in competition with the displacement of halogen by cyanide under the conditions employed for nitrile formation. In fact, for highly activated methylenes, alkylation predominates (1, 3).

The reaction of some benzyl chlorides with cyanide ion is accompanied by alkylation, especially in highly polar aprotic solvents such as *N,N*-dimethylformamide (DMF). For example, α,α' -dichloro-*p*-xylene reacts rapidly and exothermically with sodium cyanide at 100° to 110° C. to give a mixture of products, of which the major component is α,α' -dicyano-*p*-xylene (I). Distillation of the mixture removes the dinitrile, and leaves a partly tarry residue, from which can be isolated a white solid, m.p. 124° to 128° C., in 7 to 10% yield. This solid was identified as 1,2-di(4-cyanomethylphenyl)-1-cyanoethane (II) from its infrared and NMR spectra, molecular weight, and elemental analysis.

The formation of II can be explained by alkylation of I by α,α' -dichloro-*p*-xylene, with sodium cyanide functioning as base. Higher oligomers can be produced by further reaction of II.



EXPERIMENTAL

A slurry of 103 grams (2.1 moles) of sodium cyanide in 150 grams of dimethylformamide was heated to 100° to 110° C. To the heated slurry was added slowly with high-speed stirring a solution of 78 grams (0.5 mole) of α,α' -dichloro-*p*-xylene in 100 grams of dimethylformamide. The reaction mixture was cooled, when necessary, to maintain the temperature within the above range. After the addition was complete, the reaction mixture was maintained at 100° to 110° C. for a total of 8 hours. The resulting mixture was filtered hot and the insoluble material washed on the filter with hot DMF. The filtrate and washings were combined and evaporated to dryness (94.2 grams). The residue was dissolved in 200 ml. of chloroform and the solution washed successively with dilute hydrochloric acid and water. The chloroform solution was evaporated to dryness and the residue (78.2 grams) distilled under reduced pressure. The distillate consisted of 52.6 grams (0.34 mole, 67%) of α,α' -dicyano-*p*-xylene, having a boiling point of 152° to 160° C. at 0.2 mm. The undistilled residue (20.6 grams) was dissolved in benzene, the benzene solution decanted from a small quantity of black tar (1.3 grams), and the decanted solution evaporated to dryness. The residue was successively recrystallized from methanol and ethanol to yield 5.6 grams (0.02 mole, 8%) of a white crystalline solid, II, m.p. 124° to 128° C.; IR (CHCl_3): 2250 cm^{-1} ; 2260 cm^{-1} ; ($-\text{C}\equiv\text{N}$); NMR (CDCl_3): δ 7.15–7.40 (m, 8, Ar-H), 4.07 (t, 1, $J = 7.5$ Hz, NCCH_2), 3.75 and 3.77 (s, 4, NCCH_2), 3.17 (d, 2, $J = 7.5$ Hz, CH_2). Anal. calcd. for $\text{C}_{19}\text{H}_{15}\text{N}_3$: C, 79.97; H, 5.30; N, 14.73; Mol. wt. 285.33. Found: C, 79.75; H, 5.28; N, 14.45; Mol. wt. 264.

LITERATURE CITED

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